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On  
the Ethere of  
Benzoic Sulphinide.  
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A Dissertation presented  
for the Degree  
of  
Doctor of Philosophy.

by  
R. N. Brackett

1887.



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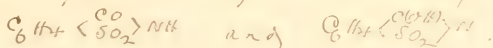




in the Ether of  
Benzoic Sulphinide.  
~~~~~

Introduction.

As stated in the American Chemical Journal Vol. 8, p. 227, the object of this investigation was primarily to determine if possible, the constitution of Benzoic Sulphinide through a study of the Ether. It is evident that according to the prevailing views in regard to the structure of anhydrides like Benzoic Sulphinide there are two formulas possible for representing the structure of this compound, namely



For, if, as has been before assumed, Benzoic Sulphinide is an anhydride, derived from (1) sulphonamine Benzoic acid by the loss of one molecule of water, plainly this dehydration may take place in two ways.



If one hydrogen atom come from the amide group and one from the hydroxyl, we represented thus:  $C_6H_4 \left( \overset{CO \cdot OH}{SO_2 NH} \right)$ , a compound of the formula  $C_6H_4 \left( SO_2 \right) NH$  containing the nitrogen in the Lactam condition would be formed. Hence as if both hydrogen atoms are furnished by the amide group, as shown by the following scheme  $C_6H_4 \left( \overset{CO \cdot OH}{SO_2 NH_2} \right)$ , a compound of the formula  $C_6H_4 \left( SO_2 \right) NH$  in which the Lactam condition exists would result.

Now, if, as assumed in a former paper on 'Benzoic Saccharinide', it is a Lactam compound and has the composition represented by the formula  $C_6H_4 \left( SO_2 \right) NH$ ; and if the salts are formed by the replacement of the imide-hydrogen by metal and hydrocarbon residues then, by making the silver salt and treating this with alkyl iodide, others should be formed of the composition  $C_6H_4 \left( SO_2 \right) N.R$ , where  $R$  = residues like methyl, Ethyl, Propyl, etc.



When benzoyl Sulphide and Phosphorus pentachloride and alcohol the reaction represented by the following equation might be expected:



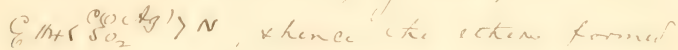
And the ether formed in these two ways, represented by the general formula



according to all our notions of structure, be identical.

If, on the other hand, Benzoyl Sulphide contains the fraction condition as expressed by the formula  $\text{C}_6\text{H}_5\text{SO}_2\text{N}^{\text{OR}}$ , then the ether formed from it by the two methods just described should be identical.

For, in this case, the silver salt would have the composition expressed by the formula



from it by treatment with alkyl iodide,

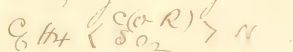




general formula  $C_6H_4\{SO_2\}^N$  is expressing their composition. While the action of Phosphorus pentachloride and alcohols might be expected to take place in accordance with the following equations



thus giving rise to an ether identical with that formed by the action of acylchlorides on the silver salt of Benzoic Sulphinide, and expressed by the general formula:



It was thus hoped, by the preparation and study of the ethers formed from the Sulphinide by these two methods, to decide between the two possible formulae for Benzoic Sulphinide





Ortho-toluene-sulphamide.

The first problem that presented itself was to find some good method of preparing Benzic Sulphinide in quantity. As the yield in Benzic Sulphinide by the oxidation of ortho-toluene-sulphamide is comparatively good, the problem resolved itself into the discovery of some method of obtaining the latter compound in quantity. The ortho-toluene-sulphamide used by Remsen and Fahlberg, when Benzic Sulphinide was discovered, was prepared by treating toluene with fuming sulphuric acid, whereby ortho- and para-toluene sulphonic acids are formed. The sulphonic acids were transformed into the calcium and then into the potassium salts, and the latter treated with phosphorus pentachloride, to obtain the chlorides which were separated by casting down the mixture to  $-15^{\circ}$ , when the para-



sulphur chloride crystallizes out, and may be  
 separated from the liquid ortho-toluene sulphur  
 chloride, and the latter transformed to the  
 amide by treatment with ammonia. This  
 method is objectionable chiefly because the  
 yield is very small, the (p)toluene sulphonic  
 acid being formed in any much the larger  
 quantity when toluene is treated with fuming  
 sulphuric acid. Kneen and Palmer (A.G.)  
 endeavored to find an improvement on this  
 method of preparing (o)toluene sulphamide  
 by starting with (p) Nitro-toluene  $C_6H_4(NO_2)(CH_3)$ . When  
 the latter compound is treated with fuming sul-  
 phuric acid the (o) sulphonic acid of (p) nitro-  
 toluene only is formed, having the composition  
 expressed by the formula  $C_6H_3 \begin{Bmatrix} CH_3 \\ SO_3H(o) \\ NO_2(p) \end{Bmatrix}$ . Now, it  
 was to be expected that when this nitro-  
 compound was reduced, and the resulting amido  
 compound transformed into the diazo com-  
 pound and the latter with alcohol, the

1) Am. Chem. Trans. Vol. 8, 242

2) Annalen 155, 8





7  
diazo group would be replaced by hydrogen,  
giving rise to (o)toluene sulphonic acid,  $\text{C}_6\text{H}_4(\text{SO}_3\text{H})$ <sup>CH<sub>3</sub></sup>.  
This (o)toluene sulphonic acid would be transformed  
into the amide, in the usual way by  
successive treatment with phosphorus pent-  
chloride and ammonia. An unexpected dif-  
ficulty arose on boiling the diazo-compound  
with alcohol. It was found that only a  
small part of the diazo compound is thus  
transformed to (o)toluene sulphonic acid, while  
in by far the larger portion the diazo group  
is replaced by the Ethoxy group,  $(\text{OC}_2\text{H}_5)$ , instead  
of by hydrogen, forming a compound of the  
formula  $\text{C}_6\text{H}_3(\text{SO}_3\text{H})$ <sup>CH<sub>3</sub></sup> in place of  $\text{C}_6\text{H}_4(\text{SO}_3\text{H})$ <sup>CH<sub>3</sub></sup>  
which was to be expected. It was therefore  
necessary to exert further for a good  
method of preparing (o)toluene sulphamide.

The method just mentioned, though it failed  
in its aim to increase the yield in (o)  
toluene sulphamide was suggestive of



step may ~~was~~ lacking to make the method  
a good one. For when p-nitrotoluene is  
treated with fuming sulphuric acid, one sul-  
phuric acid only is that the ortho is formed,  
and Remsen & Palmer had shown that the  
reduction of the nitro-compound to the amido  
compound takes place readily and with a  
good yield, and, further, that the trans-  
formation of the amido-compound to the diazo  
compound is practically quantitative. It only  
remained to find some way of replacing the  
diazo-group by hydrogen. Such a method  
was found in the work of S. Haller, who,  
in trying to obtain Pseudocumene from Pseudo-  
cumidine, by converting the latter into the  
diazo-compound & boiling with alcohol, en-  
countered the same difficulty as had Remsen  
& Palmer, the Ethoxy group entering, instead  
of hydrogen, in place of the diazo-group.  
In a private communication to Haller, as



He states in his paper on the subject, Kuiper and Lichenmann stated that when Hydrogen compounds are boiled with a ten percent solution of Copper sulphate the hydrogen group is replaced by hydrogen. By applying this method Haller succeeded in obtaining Pseudocumene. So it was determined to try this method in case of the diazo-compound in hand.

Starting with (p) nitro-toluene, this was converted into the sulphonic acid, and then through the calcium into the potassium salt as described by Bailestein and Kuchberg.<sup>2</sup> The nitro-compound was reduced to the amido-compound by suspending the finely powdered nitro compound in concentrated ammonia & passing in sulphuretted hydrogen, as described by Remsen and Palmer (A. J.).<sup>3</sup> The separation of all the sulphur from the amido compound was found to be difficult. The

1) Loc. cit.

2) Ber. 1880, 13, 1000.

3) Am. Chem. Journ. Vol. 10, 243.





transformation of the amido compound into the diazo- and then to the hydrazine compound was effected by means of a method of Victor Meyer, who obtained Phenylhydrazine by making a hydrochloric acid solution of aniline, gradually adding an aqueous solution of sodium nitrite, when the diazo-compound was formed in solution, then reducing the diazo-compound to the hydrazine by adding a hydrochloric acid solution of stannous chloride. The compound of Phenylhydrazine with stannous chloride is actually formed, by applying this method to the case in hand, and using Meyer's proportions, are introduced as follows. Ten (10) grams of (p) amido-toluene (or sulphide of potassium were placed in a Florence flask and one hundred (100) grams of hydrochloric acid added. The substance, previously finely powdered, swelled up, became crystalline. The flask was then surrounded with cold water and a solution of five (5) grams of potassium



mixture in as little water as possible, gradually added, the flask being shaken from time to time. To the solution of diazo-compound thus obtained, a solution of twenty three (23) grams of stannous chloride in an equal weight of hydrochloric acid (concentrated) was added gradually, and the flask shaken, after each addition of stannous chloride. A lustrous crystalline mass was thus obtained, which on being filtered off & boiled with water left a residue, which proved to be oxide or hydroxide of tin, undissolved. This was filtered off, and from the filtrate a substance was obtained crystallizing in glittering plates. This substance dissolves in caustic soda in the cold, producing a reddish color, and is reprecipitated by mineral acids. It reduces Fehling's solution without application of heat when a small quantity of it was boiled with a ten per cent. solution of copper sulphate. There was no reaction



of nitrogen, and precipitation of cuprous oxide as Haller found in the case of the Pseudoammonia diazo compound. The substance contains no chlorine, hence it was fair to assume, that the substance, thus obtained, was the free hydrazine compound of the formula  $\text{CH}_3\left\{\begin{matrix} \text{CH}_3 \\ \text{SO}_3\text{H} \\ \text{NH.NH}_2 \end{matrix}\right\}$ , or as further investigation lead us to believe  $\text{CH}_3\left\{\begin{matrix} \text{CH}_3 \\ \text{SO}_3\text{H} \\ \text{NH.NH}_2 \end{matrix}\right\}^*$ . From the ease with which the free compound is broken up by boiling with water, it is probable that, when the diazo-compound is reduced with stannous chloride, the crystalline mass resulting is a compound of the hydrazine with stannous chloride. A considerable amount of the hydrazine compound was prepared by the method described, using ten (10) gram portions of the azido-compound each time.

As this hydrazine compound had never been prepared or described, a short time was devoted to its study. The substance crystallizes in slightly pinkish, glistening scales or plates im-

\* The line of union between the sulphonic acid group & the hydrazine group indicates that the basic properties of the latter group are common to the former acid group.



containing no water of crystallization. It is slightly soluble in cold water, more readily in hot water, & may be purified by crystallizing from water. It acts, on the whole, like an acid, dissolving in alkalis, and being reprecipitated by the mineral acids. It is soluble in hot concentrated sulphuric acid, but crystallizes out on cooling. The substance has ~~no~~ definite melting point, decomposing from  $273^{\circ}$  -  $274^{\circ}$  (uncorr.) when it melts. From the fact that hydrazine compounds are as a rule strongly basic substances, and, since this compound acts as an acid, being soluble in many acids, hot concentrated sulphuric acid, it is probable that it has the composition represented by the formula  $\text{C}_6\text{H}_3\text{N}_4\text{O}_2$  and not  $\text{C}_6\text{H}_3\text{N}_4\text{O}_2$ .

As the hydrazine group renders a compound strongly basic, the addition of even a weak alkali to a compound constituted like this might be expected to break up the union between





than the hydrazine group & (the residue of) the sulphonic acid group, while it would require a very strong acid, like concentrated sulphuric acid to effect the same change.

\* (The formula  $\text{C}_6\text{H}_3\left\{\begin{smallmatrix} \text{CH}_3 \\ \text{SO}_3\text{H} \\ \text{NH.NH}_2 \end{smallmatrix}\right.$  is not so well in accord with the amount of nitrogen contained in the compound.) The nitrogen was determined by decomposing the hydrazine compound, and collecting the gas evolved which is pure nitrogen. Care was taken to free the apparatus from air by means of carbon dioxide. The nitrogen was collected over a previously boiled solution of caustic soda, and the last traces of nitrogen driven over by means of a current of carbon dioxide. Two determinations of nitrogen gave the following results.

Calculated for

N  $\text{C}_6\text{H}_3\left\{\begin{smallmatrix} \text{CH}_3 \\ \text{SO}_3\text{H} \\ \text{NH.NH}_2 \end{smallmatrix}\right.$   
13.86%

Found  
I 13.39% II 13.87%

\* The hydrazine compound was decomposed with a 10% solution of copper sulphate.

† omit section on hydrazine



Determination of nitrogen in the hydrazine compound gave the following numbers:

Calculated for $\text{C}_4\text{H}_3\text{N}_2\text{O}_3\text{H}_2$ $\text{N.H.NH}_2$	Found (mean of five determinations)
15.84%	15.74%

An attempt was made to prepare the Picric acid salt of this hydrazine, as described by Dr. Fischer by treating the compound with picric acid and ether. On shaking the hydrazine compound with picric acid and ether a solution was obtained. When the ether was allowed to evaporate, a residue was left, which dissolved in hot water, and on cooling a yellow flocculent substance separated. A crystallized compound could not be obtained. Attempts to prepare crystallized Barium and Calcium salts of the hydrazine compound were equally unsuccessful. Both these salts are very soluble in water and ordinary alcohol, and insoluble in absolute alcohol. Nor were efforts to obtain others



of the hydrazine any more satisfactory. Both when the hydrazine compound was suspended in absolute alcohol and hydrochloric acid gas passed in, and when it was boiled with concentrated sulphuric acid and absolute alcohol with a return condenser, the hydrazine compound appeared to remain unchanged.

In preparing the Hydrazine Compound by the method just described it was found necessary to have pure *para*-amido-toluene sulphate of sodium to start with. The yield in hydrazine has much desired, even under the most favorable circumstances, but when amido-compound containing a considerable amount of sulphur was used, no hydrazine compound was obtained in several instances. Preliminary experiments showed that the yield of *o*-toluene sulphate of sodium resulting by boiling the hydrazine compound with a ten percent solution of *o*-*para* sulphate is practically quantitative. So *o*-



Experiments were next undertaken to find, if possible, a better method of reducing the diazo compound to the hydrazine, than that of Victor Meyer. As Remsen & Palmer (1911)<sup>1</sup> had shown that the yield of diazo-compounds from the  $\alpha$ -amido-tartronic sulphate of sodium is quantitative, it was determined to prepare the diazo-compound in this way and attempt the reduction *aparte* to the hydrazine compound. Two methods of reduction were tried. In the first 10 <sup>grams</sup> of the amido compound were transformed into the diazo compound and the latter separated according to the method described by Remsen and Palmer.<sup>2</sup> The diazo compound thus formed was added gradually to a solution of twenty three (23) grams of stannous chloride in about three times the weight of hydrochloric acid. The reaction was conducted in a Florence flask, and the mixture kept cool during the operation, by surrounding the flask with cold water. An almost white crystalline

<sup>1</sup> *Ann. Chem. Phys.* Vol. 8, 243

<sup>2</sup> *Ibid.* 25



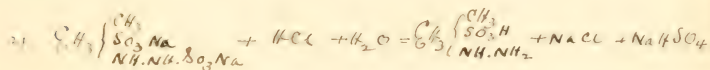
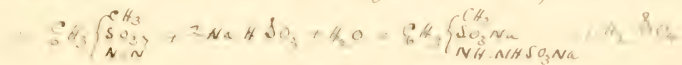


was obtained, which was thrown on a filter and the excess of hydrochloric acid driven off as far as possible with a filter-pump. The mass then treated with a considerable amount of dilute ammonia, and the precipitated tin hydroxide filtered off. From the filtrate, after driving off the excess of ammonia, the hydrazine compound was precipitated with concentrated hydrochloric acid. The amount of hydrazine compound obtained in this way was very small, being only four (4) grams. The second experiment to reduce the diazo compound by means of zinc dust and a caustic alkali was wholly unsuccessful. Failing in these experiments we had recourse to a method of Strecker and Römer, who first prepared hydrazine compounds before their nature was at all understood. Their method consists in treating a diazo-compound with an alkaline solution of sodium acid sulphite, and then precipitating the hydrazine compound with

1) Ber. D. Deutsch. Chem. Gesellschafts 14, 784 (p. 117)



concentrated hydrosulphuric acid. The reactions which take place may be represented by the following equations, in case of the diazo compound in hand:



The work from this point in the preparation of hydrazine and of (α) toluene sulphonie acid from the hydrazine compound was done in company with Mr. Csuthay. Starting with (β) nitro-toluene we prepared the sulphonie acid, and finally the potassium salt of this acid, as described by Beilstein and Kuhlberg<sup>1</sup>. It was found in the course of our work that less fuming sulphuric acid is required to transform (β) nitro-toluene to (β) nitro-toluene-ω-sulphonie acid, than is recommended by these investigators; three (3) parts by weight of fuming sulphuric acid to one (1) part by weight of (β) nitro-toluene being



23  
ficient as 4:1, as they proposed. The reduction of the nitro compound was effected by means of tin and hydrochloric acid, Mr. Kaye having found in certain preliminary experiments that the yield is better, of the amido-compound, and the reaction cleaner than when sulphuretted hydrogen is used. The reduction was conducted as follows: one (1) part by weight of the nitro-compound, one and a half ( $1\frac{1}{2}$ ) parts by weight of granulated tin (an excess) and six (6) parts by weight of concentrated hydrochloric acid were placed in a large evaporating dish. The dish was heated gently until the reaction began, then the light turned out and the dish allowed to stand, the mixture being stirred occasionally, till the reaction was over. Much heat is generated during the reduction, and the material all dissolved except some tin in excess. On cooling all the hydrochlorate of the amido-compound and some stannous chloride crystallizes out. The crystalline mass was



thrown on a filter and all the hydrochloric acid drawn off, as far as possible, with a filter-pump. The mass was then treated with ammonia to precipitate the tin & separate the amido-compound, which is soluble in ammonia. After filtering off the hydroxide of tin, the excess of ammonia was evaporated from the filtrate, and the amido-compound precipitated with concentrated hydrochloric acid. As caustic soda acts somewhat better than ammonia for precipitating the tin, this might also be used in some cases. The amido compound then obtained was transformed into the diazo compound by suspending the finely powdered substance in absolute alcohol and passing in the oxide of nitrogen (from arsenic trioxide and nitric acid), as described by Remsen and Pearson (C. 29). In converting the diazo- to the hydrazine-compound according to the method of R. Fischer and Römer.





the best results were obtained in the following way: one hundred (100) grams of diazo-compound were added gradually to 500 cc. of a cold solution of sodium acid sulphite, (prepared by saturating a solution of 2.7 parts by weight of ordinary crystallized sodium carbonate in five (5) parts by weight of water with sulphur dioxide,) (and) which had been rendered alkaline with sodium hydride. The solution turns yellow and after a considerable amount of diazo has been added, reddish yellow. After the solution has been heated nearly to boiling for about an hour, 500 cc. more of acid sulphite solution are added, and the hydrazine compound precipitates with concentrated hydrochloric acid. Even while the solution is hot, the hydrazine compound separates out, and at the same time the solution turns yellow, and there is an evolution of sulphur dioxide. On adding a large excess of concentrated hydrochloric acid, and a



the mixture to coal, it solidifies to a mass of crystals. The liquid portion was drawn off with a filter pump, and the substance washed with water, and dried in the air. The compound thus obtained is free from chlorine, and is therefore the pure hydrazine compound and not the hydrochloric acid salt of this as might have been expected. The hydrazine compound prepared, as just described, was converted into the toluene (or sulphonic acid) by boiling it with a ten percent (10%) solution of copper sulphate. The reaction which takes place may be represented by the following reaction:

$$\begin{array}{c} \text{C}_6\text{H}_5\text{SO}_3\text{H} \\ \text{NH.NH}_2 \end{array} + 2\text{CuSO}_4 + \text{H}_2\text{O} = \text{C}_6\text{H}_5(\text{SO}_3)_2\text{H} + \text{H}_2 \\ + \text{Cu}_2\text{O} + 2\text{H}_2\text{SO}_4.$$

The reaction is smooth, clean, and quantitative. The method of procedure is simple. It is may necessary to boil the hydrazine compound with the solution of copper sulphate when the above reaction takes place. It was found that when the



all the hydrazine compound had been transformed, after all evolution of nitrogen ceased, and no gas was evolved on adding a few drops more of copper sulphate solution, enough of the solution was added to color the liquid very slightly. The liquid was then filtered from the cuprous oxide, and the filtrate neutralized with Chalk. After filtering off the precipitated Calcium sulphate, the liquid was evaporated to a small volume and just enough Sodium carbonate added to precipitate the Calcium as carbonate. The filtrate, after the removal of the Calcium carbonate and Calcium sulphate carried down with it, was evaporated to dryness and the sodium tetraborate or boracic acid obtained dried on a water-bath. This salt is very soluble in water and exceedingly hygroscopic. No attempt was made to obtain it in crystalline form.

In the transformations thus far given the yield is through out good. When, however, the



attempt is made to pass from sodium toluene (or) sulphamate to (or) toluene sulphamide, there is a very great and unaccountable loss of material. The method generally used consists in treating a weighed quantity of the toluene (or) sulphamate of sodium with an equal weight of phosphorus pentachloride in an evaporating dish. On stirring the two substances, rubbing them together with a pestle, a reaction takes place, much heat is generated, phosphorus oxychloride is formed, and the mass becomes liquid. After cooling, water is added to the liquid, when the chlorides of phosphorus are decomposed, and the liquid (or) toluene sulphamchloride collects at the bottom of the dish. The supernatant liquid is then poured off and the chloride washed several times with water. Finally, water and concentrated ammonia are added, and the mixture heated on a waterbath. A light yellow colored substance, the nature of which is not





understood, is first formed and this by the further action of ammonia passes into the (o) toluene-sulphamide when all the chloride has thus been transformed to amide, and everything has gone into solution, except a little tarry matter, that is always formed in this reaction, the excess of ammonia is evaporated off, the liquid concentrated somewhat, and filtered from the tar.

From the filtrate the amide separates out on cooling in yellowish crystals, which can be easily purified by boiling with animal charcoal. The pure (o) toluene sulphamide obtained thus melts from  $152^{\circ} - 153^{\circ}$  (uncorr). However carefully the operations just described may be conducted, the yield of amide is always small; whether the loss takes place when sodium (o) toluene sulphonate is converted into (o) toluene sulphonchloride, or in the passage from the sulphonchloride to the amide was not known. Hence experiments looking to the improvement of the first transformation.



were undertaken, though variations in the method of treatment with ammonia were also tried.

In the first Experiment a weighed quantity of sodium toluene (or) sulphate was treated, in an evaporating dish, with one half ( $\frac{1}{2}$ ) the weight of phosphorus pentachloride and half ( $\frac{1}{2}$ ) the weight of phosphorus trichloride. The action is about the same as in the case of the pentachloride of phosphorus alone. The resulting chloride was washed and allowed to stand in contact with concentrated ammonia, the ammonia being renewed when used up, and the mixture frequently stirred. Stirring is necessary for other-  
 wise the yellow product formed coats the chloride, and, when this has been converted to the amide, prevents the further action of ammonia on the chloride. When the formation of the yellow product entirely ceased, the mixture was evaporated to dryness on a water-bath with ammonia. The residue is then boiled up with water



and animal charcoal, and filtered from the tarry matter. In this way seven (7) grams of pure amide melting from  $152^{\circ}$  -  $153^{\circ}$  were obtained, from 60 grams of the sulphamate.

In the second experiment, 60 grams of the sodium sulphamate and 60 grams of phosphorus pentachloride were used, and the operation conducted as in the first experiment. Sixteen (16) grams of amide were obtained.

In the third experiment 50 grams of dry powdered toluene (o) sulphamate of sodium were placed in a Florence flask, and 50 grams of phosphorus pentachloride added. When the two substances were shaken together, a violent reaction took place, much heat was generated, and hydrochloric acid and phosphorus oxychloride evolved. On cooling, the contents of the flask solidified to a brownish-black mass. The flask was then fitted with a return condenser and heated on a water bath for about two hours. The



mass remained solid, a few grams of phosphorus oxychloride were added, and the mixture heated on a water-bath for five hours. After cooling, the return condenser was replaced by one inclined and the phosphorus oxychloride distilled off on a sand-bath. To the blackish mass left in the flask, water was added and ammonia gas passed into the flask. As much heat was produced, the flask was surrounded with cold water. A black residue remained unacted upon by the gas after filtering off the residue & purifying the amide in the usual way, 8 grams were obtained. It is probable that a portion of the mass was charred in distilling off the phosphorus oxychloride on a sand-bath.

In the fourth experiment the procedure was the same as in the third, except that the phosphorus oxychloride was distilled off in an oil-bath. Although there appears to be





a good yield of Phosphine no more was obtained.

In the experiments thus far conducted no attempt had been made to regulate the temperature when the action takes place between phosphorus pentachloride and sodium sulphate of radium. In the next, fifth, experiment care was taken to regulate the temperature here, and in the other operations involved in these transformations, and in this way the best result obtained. As this appears to be the best method of preparing the chloride and amide, it will be given in some detail. Forty-five (45) grams of the radium sulphate and an equal weight of phosphorus pentachloride were placed in a Florence flask. A return condenser was then fitted to the flask and the substances mixed by shaking the flask. As soon as the reaction began, the flask was surrounded with cold water. The reaction was much less violent than in former experiments, hydrochloric acid was



given off, and the oxychloride of phosphorus  
 formed returned to the flask by the condens-  
 er. When the reaction was over, a few grams  
 of phosphorus oxychloride were added, and  
 the flask heated gently in a water-bath with  
 a return condenser for two hours. After cool-  
 ing, without distilling off any phosphorus oxy-  
 chloride, the flask was surrounded with ice-  
 water, and ice-water and a few lumps of  
 ice added to the contents of the flask. When  
 all the oxychloride of phosphorus had been de-  
 composed, the liquid (o) toluene sulphonyl chloride  
 was washed with ice water several times. Final-  
 ly, all the water was poured off, the flask  
 surrounded by ice-water, strong ammonia grad-  
 ually added to the liquid chloride, and the  
 flask shaken from time to time. The ammonia  
 acts upon the chloride readily, and very little  
 tarry matter was left. The amide separated  
 purified in the usual way, amounts to



16 grams, with a melting point lying between 152° and 153°. While the results of these experiments show no very great improvement on the ordinary method, it seems clear that the question of temperature is important, and that the best results are obtained when the temperature is kept low.

The (c) toluene sulphonamide obtained as described, was oxidized to Benzoin Sulphinide with potassium permanganate according to the method described by Remein and Fehlbey. The yield in sulphinide, as stated by these investigators, is about one half of the amide used. Something more than one half was obtained. 47 grams of amide yielding 26 grams of sulphinide. The acid potassium salt of the formula  $C_6H_4(SO_3K)$ , which they state is formed in equal quantity with the sulphinide was not so obtained. Very small quantities of it were obtained at all, due probably, perhaps,



the fact that the difference in solubility between potassium and radium chloride and their salts is not so great as stated by these in-

vestigators. All the methods thus far mentioned for preparing (o) toluene sulphinamide are long and require much time. As the sulphinide prepared was hardly enough for the experiments on the ether, it was necessary to prepare more and to find a shorter method, if possible. This end was accomplished satisfactorily by a method described some years ago by Claesson and Wallin<sup>1</sup> and recently successfully used by Noyes<sup>2</sup> for preparing (o) toluene sulphinamide. Noyes was induced to try this method because he found the same unaccountable loss in passing from the toluene(o)-sulphonic acid, through the chloride to the amide, as has been mentioned in the case.

The method of Claesson and Wallin consists in treating toluene with chlorosulphonic acid ( $\text{SO}_2\text{Cl}_2$ )

1) Ber. d. Deutsch. Chem. Gesellschaft. 12, 1888.

2) Am. Chem. Journ. Vol. 8, 176





The principal products of the reaction are *o*- and *p*-toluene sulphonyl chlorides. The substances are separated by cooling down the mixture, when the *o*-toluene sulphonyl chloride crystallizes out and may be filtered off, and the liquid *p*-toluene sulphonyl chloride drawn off and washed out by means of a filter pump. The actual method of procedure is as follows: 150 grams of Chlorosulphonic acid were placed in a Florence flask, the flask surrounded by water which was kept at a temperature of about  $10^{\circ}$ , as recommended by Placcen & Wallin and 60 grams of toluene gradually added, and the flask shaken. After all the toluene had been added, all evolution of hydrochloric acid had ceased, and the reaction was over, the contents of the flask were poured slowly into a beaker containing about a litre of cold water. The beaker was then surrounded with a freezing mixture (ice and salt, or crushed ice and concentrated hydrochloric acid), when the *o*-



Sulphochloride separates out in crystalline form. Most of the water was then poured off, and the mixture of chlorides thrown upon a filter, the liquid chloride drawn off as far as possible with a filter-pump and then the *sp* chloride washed until no more liquid chloride went through with the wash water. The liquid chloride is submitted to the freezing process until no more *sp* chloride separates out. It is impossible to remove all the *sp* chloride from the *o* chloride by this process, but, when the chlorides are converted into amides, the remainder of the *sp* compound may be separated from the *ortho* by difference in solubility in water. The *sp* toluene sulphamide being much more insoluble than the *ortho*-compound. This method of preparing *o*-toluene sulphochloride is by far the best we have found.

As it was found by preliminary experiments that the yield in amide, by treatment of



the Chloride prepared as just described, was not as good as might have been expected, Experiments were tried, looking to its improvement.

Some experiments made with *o*-toluene sulphochloride showed that the yield is nearly quantitative, and is good whether the Chloride be allowed to stand in contact with dilute or concentrated ammonia, or is heated on a water bath with ammonia dilute or concentrated.

The same experiments conducted with *o*-toluene sulphochloride mixed with a little *p*-chloride, brought out that the yield in *o*-amide is not good in any case. The best result was obtained when *o*-toluene sulphochloride was heated with dilute ammonia, 3 grams of amide being obtained from 5 grams of the chloride. - An experiment in which ammonium carbonate instead of ammonia was used gave no better result. This method is, however the best for making *o*-toluene sulphochloride



In the oxidation of the (1) telum sulphamide, which still contained a little of amide, care not having been taken to entirely separate the two, variations of the method of Remsen and Fahlberg were tried to improve the yield in Sulphinide, if possible. In the first experiment 10 grams of amide were oxidized as described by these investigators, starting with a neutral solution of potassium permanganate. The oxidation required about seven (7) hours as a result 4 grams of Benzoic Sulphinide, & 1 gram of *o*-sulphamine benzoic acid were obtained.

In the second experiment the same amount of amide and oxidizing agent were used, but the solution of permanganate was made alkaline to start with, by adding one gram of caustic potash. The oxidation took place very rapidly, the permanganate being decolorized in about two (2) hours. The yield in Sulphinide was somewhat improved, being 5.5 grams.





Residue there were obtained one (1) gram of (p) sulphamine benzoic acid and 1.5 gram of the acid salt ( $C_{10}H_{11}NO_3$ ).

In the last experiment, the oxidation was conducted in an atmosphere of Carbon dioxide. About four (4) hours were required to decolorize the permanganate. In this case from 10 grams of amide only 2.5 grams of Sulphinide were obtained, together with 1.7 grams of (p) sulphamine benzoic acid and 0.5 gram of the acid salt.

Although there was no great improvement reached in these experiments, oxidation in an alkaline solution is to be recommended as affording the best yield in Benzoic Sulphinide and being the most expeditious method.

### Preparation of Benzoic Sulphinide.

The silver salt of the sulphinide used in these experiments was prepared, as described



by Rensen and Fahlberg', by treating benzoic sulphide with dilute ammonia, boiling off the excess of ammonia, and adding silver nitrate. The silver salt of the sulphide, being insoluble in water, is precipitated as a white powder.

### Methyl Benzoic Sulphide.

After a few preliminary experiments, it was found that, the compound formed by the action of methyl iodide on the silver salt of benzoic sulphide, is best prepared in the following way.

5 grams of the silver salt and about double the weight of methyl iodide are introduced into a pressure bottle, fitted with a ground glass plate and clamp. The bottle after being tightly clamped, is placed in a water bath and heated to the boiling point of water for about two hours. Action takes place rapidly, with the formation of silver iodide, and appears to be complete in about half an hour. In order to be sure that



the action was complete, the heating was continued two hours. The bottle is then allowed to cool, is opened and about half filled with absolute alcohol. After boiling off all the excess of methyl iodide on a water-bath, the silver iodide is filtered off and washed with absolute alcohol.

The filtrate is then evaporated to a small volume. On cooling, crystals separate, which on being recrystallized from water melt from  $131^{\circ}$ - $132^{\circ}$ , and do not change in melting point after repeated recrystallization. This compound crystallizes in long flat needles. It is easily soluble in absolute alcohol and anhydrous ether, and in hot water, but difficultly soluble in cold water. It may be easily purified by crystallization from water. Three determinations of sulphur gave the following results:

I 0.18425 grams of substance gave 0.21775 grams of barium sulphate. II. 0.198415 grams of

" " were obtained from 0.169 grams.



of substance. The 0.33385 grams of substance gave 0.398515 grams of barium sulphate

Calculated for	Found		
	I	II	III
$\text{C}_6\text{H}_5\text{SO}_2\text{N}(\text{CH}_3)_2$			
16.24%	16.23%	16.13%	16.39%

The methyl compound was also prepared by the action of methyl iodide on the potassium salt of benzoic sulphinide with equally good results.

### Ethyl Benzoic sulphinide.

When the silver salt of the sulphinide was treated with Ethyl iodide, in the same way as described in the case of methyl iodide, in one experiment two well crystallized products were obtained. Both crystallize in sharp, slender radiating needles. One melted from  $83^\circ-84^\circ$ , and the other from  $96^\circ-97^\circ$ , and could not be made to melt at the same point by repeated crystallization. Both these substances are easily soluble in alcohol and hot water, less so in cold water. Both are more soluble than the methyl



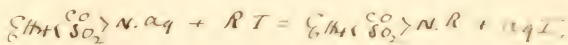


Compound. In another experiment, conducted in the same way, only one product was obtained melting from  $96^{\circ}$  to  $97^{\circ}$ . This compound is formed in smaller quantity than the methyl compound.

### Propyl Benzic Sulphide

When the silver salt of the sulphinide was treated with Propyl Iodide, a very small quantity of a crystallized substance melting at  $60^{\circ}$ - $70^{\circ}$  was obtained, and more soluble than either the methyl or Ethyl compounds.

In each of these experiments the silver iodide was formed and a crystallized compound obtained. The most natural interpretation of the reactions is expressed by the following general equation:



where  $R$  = methyl ( $CH_3$ ); Ethyl ( $C_2H_5$ ); and Propyl ( $C_3H_7$ )

Such an interpretation is accordance with the per cent of sulphur found in the methyl compound, as shown above.



Reaction of Phosphorus Pentachloride and Methyl  
Chloride on Benzene Sulphonic Acid.

By a few preliminary experiments it was found that, if benzoic sulphonic acid be mixed with an equal weight of phosphorus pentachloride and the mixture heated from 90° to 100° in a water-bath, hydrochloric acid gas is given off and the mass gradually becomes semi-fluid. On cooling it does not all solidify. If the flask in which the operation is conducted, be surrounded with cold water, and methyl alcohol added, hydrochloric acid is given off, much heat is generated and a crystalline product separates, when the crystalline product is boiled with methyl alcohol it gradually dissolves. The liquid is then evaporated to a small volume and cooling crystals separate, which recrystallized from water do not melt at 330° from the mother liquor a small quantity of crystalline material melting at 173°-125° was obtained. The latter substance is the one obtained by Rosen and



Palmer. The former substance is an acid, giving an acid reaction toward litmus paper in aqueous solution and being soluble in alcohol and reprecipitated by strong acids. The barium and calcium salts of it are more or less crystallized compounds, easily soluble in water. The analysis of the calcium salt gave the following results: 2.070 grams of the dried calcium salt gave 7.913%  $H_2O$ , and 8.95% of  $Ca$ ,  $CaSO_4$ . This compound was apparently not the ether desired so attention was turned to the compound melting at  $123^{\circ}-125^{\circ}$ .

Further experiments showed that the compound melting at  $123^{\circ}-125^{\circ}$  can be prepared in pure condition and that the reaction is tolerably clean if care be taken to regulate the temperature in all the operations involved. The best result was obtained in the following way: 5 grams of benzoic disulphide and an equal weight of phosphorus pentachloride were placed in a small Erlenmeyer flask fitted with a cork through



which passed a long glass tube to conduct off the hydrochloric acid gas evolved during the reaction. The flask was heated in a water-bath at  $70^{\circ}$ - $75^{\circ}$ . The reaction began between  $65^{\circ}$  and  $70^{\circ}$ . The heating was continued two hours when the mass became semi-fluid and all evolution of hydrochloric acid gas ceased. On cooling all did not solidify. The flask was then surrounded with a freezing mixture (crushed ice and concentrated hydrochloric acid), and methyl alcohol added gradually from a drop-funnel: when the addition of a little methyl alcohol ceased to produce an evolution of hydrochloric acid gas, the crystalline product which had separated, was heated with methyl alcohol, at the boiling point of the latter, for about an hour. The flask was then surrounded with a freezing mixture and crystals were deposited, which, on being separated, melted at  $123^{\circ}$ - $125^{\circ}$ . After recrystallizing the compound several times from water, the





melting point rose to  $125^{\circ}$ - $126^{\circ}$ , and did not change, when the compound was recrystallized several times. From the mother liquor, after evaporating to a smaller volume, more of the compound melting at  $125^{\circ}$ - $126^{\circ}$  was obtained. If the operations are conducted as described, none of the compound melting above  $330^{\circ}$  is formed, and a good yield of the compound melting at  $125^{\circ}$ - $126^{\circ}$  can be obtained.

The compound melting at  $125^{\circ}$ - $126^{\circ}$  crystallizes in radiating needles. It is easily soluble in alcohol, ether and hot water. It is difficultly soluble in cold water and may be easily purified by recrystallization from water. Determination of Sulfur and Nitrogen gave the following results:

I 0.2939 grams gave 0.298915 grams  $\text{BaSO}_4$

II 0.1000 " " 0.100715 "  $\text{BaSO}_4$

The nitrogen was determined by Kjeldahl's method and 0.12225 grams of substance used.



Calculated for		Found	
$C_8H_4(SO_2)NCH_3$ or $C_8H_4(SO_2)_2N$		I	II
S	16.24 %	13.87%	13.83%
N	7.11 %	5.74%	—

Further, we have here a substance that is neither isomeric nor identical with the methyl compound prepared from the silver or potassium salt of the sulphinide and methyl iodide.

Further study of the substance showed that when boiled with water and barium carbonate, it forms a salt that corresponds very closely with the barium salt of the sulphinide. This salt crystallizes in needles of a silky appearance, is easily soluble in water, and has the characteristic sweet taste of the barium salt of the sulphinide. An analysis of the air dried salt gave 12.89% of water and 23.42% of barium sulphate.

Calculated for		Found	
$C_8H_4(SO_2)N_2Ba + 4H_2O$			
Ba	23.59%		23.42%
4 H <sub>2</sub> O	12.66%		12.89%



That this is really the barium salt of the sulphide was confirmed by the fact that the sulphide can be obtained from it by treatment with hydrochloric acid.

The only compound that could be formed from the sulphide by the action of phosphorus pentachloride and methyl alcohol with the per cent of sulphur found, is one of the formula,  $C_6H_4\left\{\begin{smallmatrix} COCH_3 \\ SO_2 \end{smallmatrix}\right\}_2NH$ . Such a compound would contain 13.97% of sulphur, while 13.87% were found. A compound analogous to this was obtained by Stokes<sup>1</sup>, by the action of phosphorus pentachloride and methyl alcohol on the potassium salt of Phthalic Sulphinide. The chloride obtained had the composition represented by the formula:  $C_6H_3\left\{\begin{smallmatrix} SO_2 \\ Cl \end{smallmatrix}\right\}_2N.PoCl_2$ , and the ether that represented thus:  $C_6H_3\left\{\begin{smallmatrix} COCH_3 \\ COOCH_3 \end{smallmatrix}\right\}_2NH$ . So the formation of such a compound in the case of Benzoic Sulphinide is at least possible.



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Chloride of Benzoic Sulphinide.

In order to confirm the supposition in regard to the compound melting at  $125^{\circ}$ - $126^{\circ}$ , attempts were made to isolate and analyze the chloride formed by the action of phosphorus pentachloride on the sulphinide. It had been found that, when the semi-fluid mass formed in the reaction is cooled down with a freezing mixture, a crystalline product separates on the addition of methyl alcohol. On one occasion this crystalline product was filtered off, without first boiling it with methyl alcohol. On boiling it with water to recrystallize it the sulphinide was obtained, and no methyl compound. This was very probably the chloride. On preparing some of it in the way described, it was found to contain chlorine. An attempt was made to recrystallize it from petroleum ether, but it was found to be very slightly soluble. After boiling with petroleum ether





the compound was sweet, though it still contained chlorine. Fearing, however, that some decomposition had taken place no analysis was made.

A second attempt was made to isolate the chloride, in which anhydrous ether was substituted for methyl alcohol, in order to avoid any possibility of the formation of any of the methyl compound. The crystalline product was carefully washed repeatedly with anhydrous ether to remove all the phosphorus oxychloride, then placed over calcium chloride in a desiccator. Determinations of chlorine gave varying results and none that agree with a chloride of the formula  $C_6H_4 \begin{Bmatrix} CCl_2 \\ SO_2 \end{Bmatrix} N \cdot POCl_2$ . Owing to the lack of material no more attempts were made to isolate the chloride.

In spite of the fact that a pure chloride could not be obtained, the formation of an ether agreeing so well with one repre-



erited by the formula  $C_6H_4(SO_2)^{O(C_6H_5)_2}NH$ , and the fact that the chloride obtained actually contains phosphorus, make it very probable that a chloride of the composition represented by the formula  $C_6H_4(SO_2)^{O(C_6H_5)_2}N.PoCl_2$  is formed (though it could not be separated).

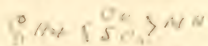
### Conclusion.

The facts brought out in this investigation, plainly require further work before a perfectly satisfactory explanation of them can be given. Thus far all the facts, save one can be explained more satisfactorily on the assumption that Benzoin Sulphinic has the composition represented by the formula  $C_6H_4(SO_2)^{O}NH$ , than on the other possible formula  $C_6H_4(SO_2)^{O(OH)}N$ . The one exception opposes both of these formulas, and lies in the fact that, when the methyl compound obtained by the action of methyl iodide on the silver or potassium salt of the sulphinic



also is treated with barium hydroxide a soluble  
 barium salt is formed, which when treated with  
 hydrochloric acid yields the methyl compound  
 again. It was hoped that the methyl compound  
 would then be saponified, and had the methyl  
 compound from the phosphorus pentachloride  
 reaction, but this was not the case. And, if  
 the methyl compound has the composition rep-  
 resented by the formula  $C_6H_4(SO_2)N.OH$ , it is  
 impossible to see how a barium salt could  
 be formed, without the compound first under-  
 going saponification.

Owing to lack of time and material  
 the work had to be abandoned at this stage.  
 The question as to the exact nature of Ben-  
 zic sulphinate is far from satisfactorily  
 settled. But, as stated, all facts, save one,  
 point to the formula



as representing its composition.















